

Refractory shaped body with increased alkali resistance

The invention relates to a refractory batch and to a process for its production.

Refractory materials which are used for lining kiln and furnace vessels and chambers are often subject to high chemically corrosive loads from alkaline metal salts of a complex composition. This chemically corrosive load prevails in particular in a temperature range from 700 to 1300°C.

The origin of the salts is complex. Both the material being fired and the fuels often liberate alkali metals. These alkali metals are known to form low-viscosity salts in the corresponding temperature range and act as fluxes, i.e. agents which reduce the melting point, in most refractory or ceramic systems.

In the cement industry, for example, the alkali metals originate in part from the - in particular clay-containing - raw materials. Furthermore, the alkali load has risen considerably on account of the fuels which are in use nowadays. Particularly when firing the cement clinker in rotary tubular kilns, the fuel has been changed from relatively clean natural gas and oil to lower-quality coals and waste fuels, such as rubber tires, waste oils, plastics and solvents. These fuels have the advantage of being favorable given a sufficient energy content and, moreover, of being thermally disposed of, as remainder materials, at the temperatures which prevail in the rotary tubular kilns. However, the chemically corrosive wear caused by volatile substances, such as complex alkali metal salts, which escape or are formed during the combustion has risen drastically. These chemically corrosive,

complex salts substantially comprise: K^+ , Na^+ , O^{2-} , SO_3^{2-} , Cl^- , OH^- , F^- , S^{2-} . Depending on the molar ratio, the chemically corrosive salts which are formed substantially comprise the following individual components: K_2SO_4 , Na_2SO_4 , Na_2O , K_2O , $NaOH$, KOH , KCl , $NaCl$. The oxygen partial pressure and the molar ratio of alkali metal oxides to SO_3 have a further influence on the composition of these salts. For example, at a low oxygen partial pressure sulfides are formed, while at a high oxygen partial pressure the corresponding sulfates are formed. If the molar ratio of alkali metal oxide to SO_3 is below 1, alkali metal oxide is formed as well as alkali metal sulfate, while if the molar ratio is above 1, SO_2/SO_3 is formed as well as alkali metal sulfate.

The temperature range from 700 to $1300^{\circ}C$ is particularly critical, since the alkali metal salts, which are usually volatile at over $1300^{\circ}C$, are deposited on the refractory lining within this temperature range, and then infiltrate and corrode this lining. Under the action of the temperature gradient, this infiltration and corrosion takes place to a very great depth, in many cases even down to the metallic kiln shell. Therefore, particularly in the case of a rotary tubular kiln, the kiln section or the refractory lining of the kiln section in which the temperatures are between 700 and $1300^{\circ}C$ is subject to a particularly high load. The corrosion processes are, firstly, the infiltration, the infiltration by the alkali metal salts causing the microstructure to be compacted and become brittle and, moreover, the bonding is loosened by the crystallization pressure. This results in premature wear on account of hot abrasion and flaking. Furthermore, the increase in thermal conductivity, in conjunction with the wear mechanism described above, allows dangerous overheating of the metallic kiln shell.

Moreover, chemical corrosion takes place, in which the infiltrates react with the primary phases of the refractory lining, so as to form new, secondary phases with a low melting point, in particular melting points which are lower than the actual application melting point. Furthermore, volumetric expansion can be observed. Overall, therefore, the wear caused by chemical corrosion takes place through melting, hot abrasion and also flaking.

It is known to use refractory shaped bodies with Al_2O_3 contents of 40 to 60% by weight in the safety and preheating zones of rotary kilns used in the cement industry.

Both natural and synthetically produced raw materials, i.e. in particular natural raw materials from the sillimanite group, bauxite and refractory clay, can be used for the production of high-alumina bricks, as are used in particular in the abovementioned field of rotary tubular kilns in the cement industry. Suitable synthetic raw materials are sintered mullite, fused mullite, calcined alumina, sintered corundum and fused corundum. Numerous attempts have already been made to improve the alkali resistance of refractory products from the $Al_2O_3-SiO_2$ system, in particular in the cement sector.

DE 36 33 816 relates to a refractory composition for the production of refractory bricks which are said to have a high resistance to alkaline attack. The material described is to have a minimum alumina content of 60% by weight. It is stated in that document that one of the solutions for improving the alkali resistance is to reduce the alumina content from a minimum of 60% by weight to 50% by weight. 50% by weight of SiO_2 would then be added to this 50% by weight of Al_2O_3 . However, this is highly detrimental to the refractory properties of the brick, so that overall, although the alkali

resistance is improved, the refractory strength becomes unsatisfactory. To increase the alkali resistance, high-alumina bricks containing 60% by weight of alumina were mixed with zirconium, phosphorous acid, titanium dioxide and boric acid. Moreover, tests were carried out with a relatively small amount of silicon carbide. In this document, it is stated that the addition of zirconium, titanium dioxide and boric acid leads to only a slight improvement in the alkali resistance, while the addition of phosphorous acid (phosphate bond) resulted in an improvement in the resistance, although not a particularly great improvement. By contrast, the addition of silicon carbide led to a considerable improvement in the alkali resistance of the mixture. It is explained in this document that even adding 10% by weight of the silicon carbide leads to a considerable improvement. However, it is pointed out that the silicon carbide has to be added in the fine fraction or to the matrix of the mixture (< 0.2 mm). Furthermore, it can be seen from Table 2 of this document that the phosphate bond, in combination with the addition of SiC, has an adverse effect on the alkali resistance.

US 5,382,555 has disclosed a refractory shaped body which contains at least 50% by mass of Al_2O_3 , in which metal carbide particles are to be present in an amount of from 3 to 25% by mass. The subject of this document is also the improvement in a shaped body with a high alumina content in terms of its resistance to molten slags; this brick is supposed to be substantially free of what are referred to as "black cores". These "black cores" are the result of incomplete oxidation of the carbon in the shaped body or in the raw material. These "black cores" not only have esthetic drawbacks, but also have undesirable properties, in particular a reduced ability to withstand temperature changes and a tendency to flake in use. This is attributable to inhomogeneities in the microstructure. This document proposes producing a mixture in such a manner that the

fired product has a refractory, clay-bonded basic batch with a high aluminum content, the intention being for the alumina content to be at least 50%; moreover, metallic carbide, in particular silicon carbide, is added in amounts of from 3% to 25%, although under no circumstances should more than 1.5% of metal carbide < -325 mesh (45 μm) be added.

Therefore, the prior art and previous specialist knowledge state that SiC should not be used together with a phosphate bond and that, moreover, only an extremely small amount of fine SiC should be added to refractory shaped bodies, since otherwise "black cores" are formed, with negative consequences.

Despite the extensive literature cited above, which describes refractory shaped bodies containing SiC, shaped bodies of this type have no role whatsoever on the commercial market, since their properties are impossible to control. Although SiC-containing shaped bodies are marketed under the tradename Carsial, they have very high SiC contents, in the range from 43 to 90%.

It is an object of the invention to provide a batch and a refractory shaped body produced therefrom which has an improved alkali resistance.

The object is achieved by a batch having the features of claim 1; advantageous refinements are described in the subclaims.

A further object is to provide a process for producing the batch and shaped body. This object is achieved by the features of claim 8; advantageous refinements are given in the subclaims which are dependent on this claim.

The invention is explained by way of example with reference to a drawing, in which:

Figure 1 shows the grain size distribution and the cumulative curve of the grain size distribution of the SiC used according to the invention,

Figure 2 shows a shaped body according to the invention with cut-in crucible, in cross section after alkali attack from K_2O ,

Figure 3 shows a comparison shaped body without SiC after the alkali attack, which has been completely destroyed by alkali attack.

According to the invention, it has been discovered that, surprisingly, with a batch or shaped body made from this batch which contains 40% to 60% of Al_2O_3 and 3% to 15% of finely particulate SiC, the alkali resistance can be dramatically improved if a phosphate bond is used. This is even more surprising since it has hitherto been assumed that the addition of finely particulate SiC, on the one hand, and the phosphate bond, for example produced by phosphoric acid or monoaluminum phosphate, in combination with SiC, on the other hand, has major drawbacks for refractory shaped bodies or batches.

According to the invention, contrary to previous specialist opinion, more than 1.5% of SiC of $<0.045\text{ mm}$ is added, approx. 75% of the SiC added lying in the range $<0.045\text{ mm}$. Overall, therefore, at least 2.3% of the SiC, based on the quantity of the total batch, is below 0.045 mm, given an addition of 3% based on the total mass. Tests have established that even in the refractory shaped body produced according to the invention "black cores" may form. Surprisingly, however, it has been established that, in the shaped

body according to the invention, these "black cores" do not cause any microstructural inhomogeneities which are such that this "black core" would cause weakening of the microstructure. The reason for this is not currently clear.

The invention is explained below with reference to an example. A high-alumina raw material containing 51% by weight of Al_2O_3 with a maximum grain size of 4 mm and a grain size distribution corresponding to a typical Fuller curve is mixed with 5% of a refractory binding clay, the mixture including 5% of SiC with a grain size of from 0 to 0.9 mm. This mixture is mixed with the quantity of phosphoric acid which is usually required as binder component. After mixing to homogeneity, the mixture obtained in this way or the batch obtained in this way is pressed under a pressure of 90 MPa. Then, the shaped bodies obtained are dried at temperatures of over 100°C, in particular 120°C, and, after subsequent drying, are fired at a sintering temperature of approx. 1260°C. For comparison purposes, a brick is produced in the same way, except that, instead of the silicon carbide, the high-alumina, refractory raw material or the refractory main component is added in the grain size which corresponds to the SiC. After firing, both shaped bodies have a homogeneous appearance and a homogeneous microstructure. There was no "black core" in the silicon carbide brick.

After firing, crucibles which have an edge length of 70 mm and an internal bore with a diameter of 40 mm were cut out of the two bricks in accordance with DIN 51069. To simulate alkali attack, these crucibles were filled with 70 g of potassium carbonate. The crucibles were then closed off with a cover made from the same material and were treated in a kiln for five hours at a temperature of 1100°C.

The result after firing is that the SiC-free shaped body has been greatly destroyed by the alkali attack (Figure 3) and has large cracks. The microstructure reveals considerable infiltration.

By contrast, the brick containing 5% of finely particulate SiC and a phosphate bond (Figure 2) does not reveal any effect on the microstructure through the alkali attack. The shaped body is free of cracks. The alkali resistance of the shaped body according to the invention is, surprisingly, so high that potassium carbonate has boiled over out of the crucible, since it was unable to penetrate into the microstructure of the brick.

The mechanism which leads to the dramatic increase in alkali resistance observed has not thus far been determined.

An advantage of the shaped body according to the invention is that it has an extremely high alkali resistance, so that it can be used wherever high concentrations of alkali occur in a high-temperature process. This includes, for example, preheating, safety and transition zones of rotary tubular kilns used in the mineral processing industry and also sintering zones in kilns of this type with moderated temperature stresses.